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P. R. MALLORY & CO. INC.

Indianapolis, Indiana

P. R. MALLORY & CO. INC.
CORPORATE CHEMICAL RESEARCH LABORATORIES

MERCURY CELL BATTERY INVESTIGATION

Contract No. AF 33(657)-7706
Project No. 8173, Task No. 817304-14

QUARTERLY TECHNICAL PROGRESS REPORT
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Prepared by: R. E. Ralston

FOREWORD

This report was prepared by P. R. Mallory & Co. Inc., Indianapolis, Indiana, for the Aeronautical Systems Division of Wright-Patterson Air Force Base, Ohio, on Contract No. AF 33(657)-7706 under Task No. 817304-14 of Project No. 8173. It is our pleasure to acknowledge the assistance of Messrs. W. Bishop and J. Cooper, Project Engineers of the Aeronautical Systems Division.

Three Quarterly Progress Reports and a Final Report were issued during the initial contract period. The Final Report contained data obtained during the fourth quarter, consequently, this report is designated Quarterly Technical Progress Report No. 5.

The work covered by this report was accomplished under Air Force Contract No. 33(657)-7706, but is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

TABLE OF CONTENTS

I. INTRODUCTION	<u>Page</u> 1
II. FACTUAL DATA AND DISCUSSIONS	2
A. Positive Electrode	2
1. Addition of Precious Metal Catalysts	2
2. Addition of Organic Binders	3
3. Matrix Materials	3
B. Negative Electrode	4
C. Instrumentation	6
III. SUMMARY	7
IV. PROGRAM FOR NEXT INTERVAL	7

ABSTRACT

The charge acceptance of the positive electrode is improved by the addition of catalysts such as palladium, platinum and rhodium. Sintered silver plaques, amalgamated to form positive electrodes, have not increased performance. The replacement of silver in this electrode with gold improves charge acceptance efficiency.

Sintered silver plaques impregnated with zinc amalgam to form negative electrodes have been cycled. Electrodes of this type have not accepted complete recharge at the normal electrode charging voltage.

Initial attempts to employ a capacitance measuring technique to indicate surface area of porous electrodes are encouraging. Porous silver electrodes have exhibited fairly stable films in KOH electrolyte for evaluation, while porous nickel films have been less stable.

I. INTRODUCTION

This program provides for continuation of the analytical and experimental applied research on the zinc/potassium hydroxide/mercuric oxide-silver electrochemical system which was initiated under Air Force Contract Number 33(657)-7706. The objective of this program is to provide design criteria and establish technology for a long life, lightweight mercury cell battery for aerospace applications.

The applied research will include, but not limited to, the following areas: (a) investigate methods for increasing low temperature (down to 0°F) capability of the mercury cell battery, (b) conduct an investigation to determine if a satisfactory separator material for the zinc-mercuric oxide system exists, (c) investigate methods of improving the high rate characteristics of the electrodes (up to 500 ma/cm²) with a minimum reduction in cycle life and discharge terminal voltage, and (d) conduct a detailed investigation toward elimination of dendritic growth of zinc crystals on the negative electrode. Some of the goals this program will be directed toward accomplishing are:

1. The battery shall be capable of 20 ampere discharge for 35 minutes with voltage maintained at 27.5 volts, +3.0, -1.5 volts.
2. The battery will be capable of storing sufficient energy in 55 minutes to satisfy the requirements of (1) above.
3. The battery shall be capable of repeated cycling to a goal of 25,000 cycles which operating in a temperature range of 0°F to 140°F.
4. Minimum weight (goal: 10 pounds) and minimum volume should be considered.
5. The battery shall be capable of operation in any position, in zero gravity environment, in a vacuum of 10⁻⁹ mm of Hg, and without maintenance throughout its entire cycle life.

Accomplishments toward meeting the above goals are reported in subsequent sections of this report.

II. FACTUAL DATA AND DISCUSSIONS

A. Positive Electrode

It became apparent during the first years work that a battery composed of cells discharging at the Zn-Ag₂O voltage level and then the Zn-HgO voltage level during the same cycle would not remain within the contract voltage regulation requirement of 27.5 ± 1.5 volts. Nor will it meet the present contractual requirement of 27.5 ± 1.5 volts. To meet this discharge voltage the individual cells in a battery would have to operate as follows:

22 cell battery: 1.385 volts maximum, 1.18 volts minimum

23 cell battery: 1.326 volts maximum, 1.13 volts minimum

24 cell battery: 1.27 volts maximum, 1.083 volts minimum

In order to obtain a more constant discharge voltage, ie, absence of Ag₂O voltage, the charging voltage must not be allowed to reach the Ag₂O formation voltage. The maximum allowable charging voltage has been established at 1.50 volts. Since the optimum charge acceptance current density of the positive electrode will apparently dictate the electrode area needed to produce the required output, considerable effort has been placed on charge acceptance evaluations at this low voltage. Studies have included the effects of palladium and other precious metal catalysts, organic binders, and matrix materials.

1. Addition of Precious Metal Catalysts

Palladium-containing electrodes have been under investigation from the standpoint of electrode potential during the charging operation. The presence of palladium produces a lower potential throughout the charging operation with no evidence of AgO formation (as measured by X-ray diffraction) prior to gas evolution. Conversions of mercury to HgO and silver to Ag₂O to the extent of 80%-85% of theoretical have been obtained when charging continued through the silver oxide formation voltage without regard to discharge voltage regulation. Further evaluations, with the charging operation stopped below the silver oxide formation voltage, ie, to 1.50 volts, have shown a considerable decrease in charge acceptance. At the present time efficiencies in the range of 20% to 30% are being obtained. This is based on conversion of the mercury to HgO in an electrode nominally composed of 69% Hg-31% Ag.

Most of these investigations have been performed in an exploratory research cell having an electrode area of 0.235 in² under uninhibited conditions (ie, excess electrolyte and no separators). A HgO-Hg-Ag reference electrode was employed to facilitate half cell voltage readings. In general, complete cycles were used to determine the

charge acceptance. Electrodes were charged to either 1.5 volts or 2.0 volts and then discharged below 0.9 volts.

Other catalysts, namely platinum and rhodium, have also been incorporated in the positive electrode. This has been accomplished by electroplating the silver powder with either platinum or rhodium, using a commercial plating solution, followed by mercury addition to produce the desired alloy. Both platinum and rhodium produce increased charge acceptance when compared to the 69% Hg-31% Ag electrode without additives. However, there is evidence that both materials cause gas discharge at the positive electrode.

Data shown graphically in Figures 1, 2, 3 and 4 were obtained (1) without catalyst added, (2) with palladium added, (3) with platinum added, and (4) with rhodium added.

2. Addition of Organic Binders

While the addition of palladium produces higher charge acceptance, it does not minimize the gradual decrease in charge acceptance encountered during cycling. In an effort to overcome this condition, positive electrodes containing polyethylene oxide as an expander were evaluated. This material was incorporated by coating an expanded silver with a paste prepared by mixing powdered 69% Hg-31% Ag material with polyethylene oxide and water. Being water soluble and insoluble in KOH, the polyethylene oxide forms an electrolyte permeable matrix but decreases the rate of diffusion enough to lower charge acceptance. Figure 5 shows charge acceptance data for a positive electrode containing 0.17% platinum and 2% polyethylene oxide.

3. Matrix Materials

In an effort to further increase charge acceptance, positive electrodes prepared by amalgamating sintered silver plaques are being investigated. The desired mercury content is evenly distributed on the silver electrode by electroplating. Palladium has been incorporated in some electrodes prior to the amalgamation process. In general, these approaches have produced charge efficiencies in the range of 20% (based on the mercury content) with the charging voltage limited to 1.5 volts.

These data, combined with comparable results obtained with compacted powder electrodes, seem to indicate that the rate limiting reaction in the charging operation of the positive electrode is the diffusion of mercury in silver. The ease with which silver oxidizes in this environment and the surface area (or particle size) of the electrode are also contributing factors. The charging operation proceeds by increasing voltage increments, the characteristics of which depend on the current density and the presence or

absence of palladium (or other catalyst). The mercury conversion voltage prevails until the terminal voltage reaches 1.5 volts. From this point the voltage gradually increases toward the silver conversion voltage. During this portion of charge less mercury is available on the electrode surface for oxidation and the formation of Ag_2O begins. A reaction between Ag_2O and Hg to form HgO and Ag proceeds during charge and on idle stand. This is evidenced by the Ag_2O -Zn potential obtained when a cell is discharged immediately upon removal of the charging source. But during an idle stand period the Ag_2O -Hg reaction continues toward completion and the HgO-Zn potential is obtained on discharge (provided the input charge is less than the theoretical capacity of the mercury in the electrode). If the charging operation is continued Ag_2O can be converted to AgO.

The effect of idle stand in the discharged state is shown by cycle 20 of Figure 2. It is assumed that during the 60 hour stand time the mercury diffused into the silver to cause the decrease in charge acceptance recorded for this cycle. An increase in charge acceptance at the 1.5 volt level usually follows a "deep" cycle of charge to high voltage. This is probably due to the mercury-rich coating each silver particle obtained during the previous high capacity discharge. Upon continued cycling this increased charge acceptance obtained after a deep cycle gradually declines. During these electrode evaluations no attempt has been made to establish an optimum cycle depth for extended cycle life.

Since the oxidation characteristics of silver are detrimental with respect to discharge voltage regulation, investigations with an amalgamable material of poor oxidizing ability was initiated. Electrodes consisting of several gold-mercury alloys have been evaluated. The 31% Au-69% Hg ratio contained a liquid phase and polarized rapidly on charge. Two alloys near the 50% Au-50% Hg composition gave approximately 33% charge acceptance, based on the mercury content. The alloy 57.8% Au, 41.6% Hg, 0.6% Pd gave 57% charge acceptance at 64 ma/in² (equivalent to the 100 ma/in² discharge rate in a 90 minute orbit). While these investigations are considered cursory, the efficiency exhibited by the gold matrix electrode is approximately double the efficiency obtained with the 69% Hg-31% Ag electrode when charged below the silver oxide formation voltage. Apparently the diffusion rate of mercury in gold is now the limiting reaction since the oxidation characteristics of silver have been removed.

B. Negative Electrode

It was determined during the first years work that a high mercury-zinc negative electrode (approximately 90% Hg-10% Zn) was capable

of high rate discharge when used with the retaining member designed, but since the electrode area required in a cell designed to meet contractual requirements will be governed by the charge acceptance of the positive electrode, a high rate capability of this electrode is not required. Toward development of a more simple structure with area equivalent to the positive electrode, negative electrodes prepared by impregnating sintered silver plaques with 90% Hg-10% Zn alloy are being investigated. Efforts have been in the areas of plaque preparation, surface area measurements (described under Instrumentation below), impregnation, and evaluation.

Sintered silver plaques are being prepared by the reduction of silver oxide. Dry silver oxide powder is spread evenly over expanded silver screen without applying pressure. Plaques are sintered in air at 400°C for 30 minutes. No other mechanical operations have been employed.

Attempts are being made to obtain a measure of surface area by capacitance measurements. Early indications are that reproducible values can be obtained with porous silver electrodes, but since techniques and equipment are not finalized, numerical data will not be presented.

Electrodes have been impregnated by immersion in molten 90% Hg-10% Zn alloy at 110°C. The amount of zinc incorporated in electrodes of one square inch was equivalent to 117 ma-hrs. These were placed between two charged positives with separators in place to produce cells which simulate actual operating conditions for evaluation. The data in Table I were obtained with a negative electrode composed of 0.142 g. zinc (117 ma-hrs.), 1.282 g. mercury, and 0.975 g. sintered silver electrode.

TABLE I

Negative Electrode Experiments

Cycle No.	Discharge			Charge		
	Rate (ma/in ²)	Time (min.)	Capacity (ma-hrs)	Rate (ma/in ²)	Time (min.)	Capacity (ma-hrs)
1	100	21	70.0	65	32	70.0
2	100	22	73.2	65	25	54.1
3	100	13	43.4	32.5	50	54.2
4	50	29	48.4	--	--	--

These results are characteristic of several other electrodes made in the same manner. The voltage measured between the anode and reference electrode during charge increased above normal. Under

most conditions the anode vs. HgO-Hg-Ag reference electrode voltage remains within 1.38-1.42 volts, while values up to 1.66 volts were obtained with electrodes of this type. High anode voltages on charge sometimes result when the anode discharge reaction product is not readily available at the surface during charge.

A negative electrode of equal dimensions was prepared by applying a paste consisting of electrolyte, zinc oxide, mercuric oxide, and polyvinyl alcohol to expanded silver screen. Evaluations were conducted in a like manner.

TABLE II

Negative Electrode Experiments

Cycle No.	Charge			Discharge		
	Rate (ma/in ²)	Time (min.)	Capacity (ma-hrs)	Rate (ma/in ²)	Time (min.)	Capacity (ma-hrs)
1	65	60	114*	100	31	103
2	65	53	115	100	35	117
3	65	50	108	100	31	103
4	32.5	80	80	50	51	85

* 16 ma-hrs was required to reduce the mercuric oxide in the electrode.
Reference voltage measurements on charge were normal with this electrode.

C. Instrumentation

The evaluations of sintered electrodes as a matrix for both positive and negative electrodes has brought forth a need for a simple method of surface area indication. It was considered that the relationship between electrode capacitance and surface area could be determined and used to obtain a measure of surface area. The justification for this is based on the tendency of most metals to form surface coatings when immersed in an electrolyte. The degree of electrical isolation measured by capacitance measuring methods will depend on the metal, the electrolyte, and the dielectric constant of the film. It must be assumed that the measured capacitance is proportional to the surface area and that the characteristics of the surface film of a porous electrode are identical to those of a smooth surface electrode. After the capacitance of an electrode of unknown area has been determined, the measured value of a known area, smooth surface electrode is used to calculate the unknown area by the following expression:

$$\frac{mfd}{\text{Unit Area}} = \frac{mfd \text{ (measured)}}{\text{Unknown Area}}$$

In order to eliminate cathode capacitance error, measurements are being made on two electrodes "back to back". This cell arrangement is considered to represent two capacitors in series and calculations must be made accordingly. For instance, when two smooth surface electrodes 0.50" x 2.0", having a surface area of 2 in² each (counting both surfaces), are measured the value obtained represents capacitance per square inch directly.

Initial measurements to prove feasibility and establish techniques have been made with a Wein type capacitance bridge which lacks sufficient range and balance definition for extreme accuracy. A bridge with more range and accuracy will be available during the next period. Additional work is required in the areas of material cleaning techniques required prior to measurements and stability of the surface film being measured. Early indications are that capacitance measurements will offer an approach to surface area determinations.

III. SUMMARY

The effect of rhodium and platinum addition to positive electrode material has been studied. These materials increase charge acceptance, but results have not shown any improvement over the characteristics of palladium.

The charge acceptance of the positive electrode at the mercuric oxide level can be increased from the 30% efficiency level to a 55% level by replacing silver matrix material with gold.

Negative electrodes prepared by amalgamating sintered silver plaques with a 90% Hg-10% Zn alloy have been investigated. Cycles were characterized by low efficiencies on discharge and half-cell voltages above normal on charge.

Capacitance measuring techniques to indicate surface area of porous electrodes appear feasible.

IV. PROGRAM FOR NEXT INTERVAL

1. Continue with positive electrode evaluations toward improving charge acceptance at the mercuric oxide level.
2. Investigate negative electrodes prepared by electrodeposition of zinc and mercury on sintered silver.
3. Continue surface area evaluations of porous electrodes by capacitance measuring techniques.

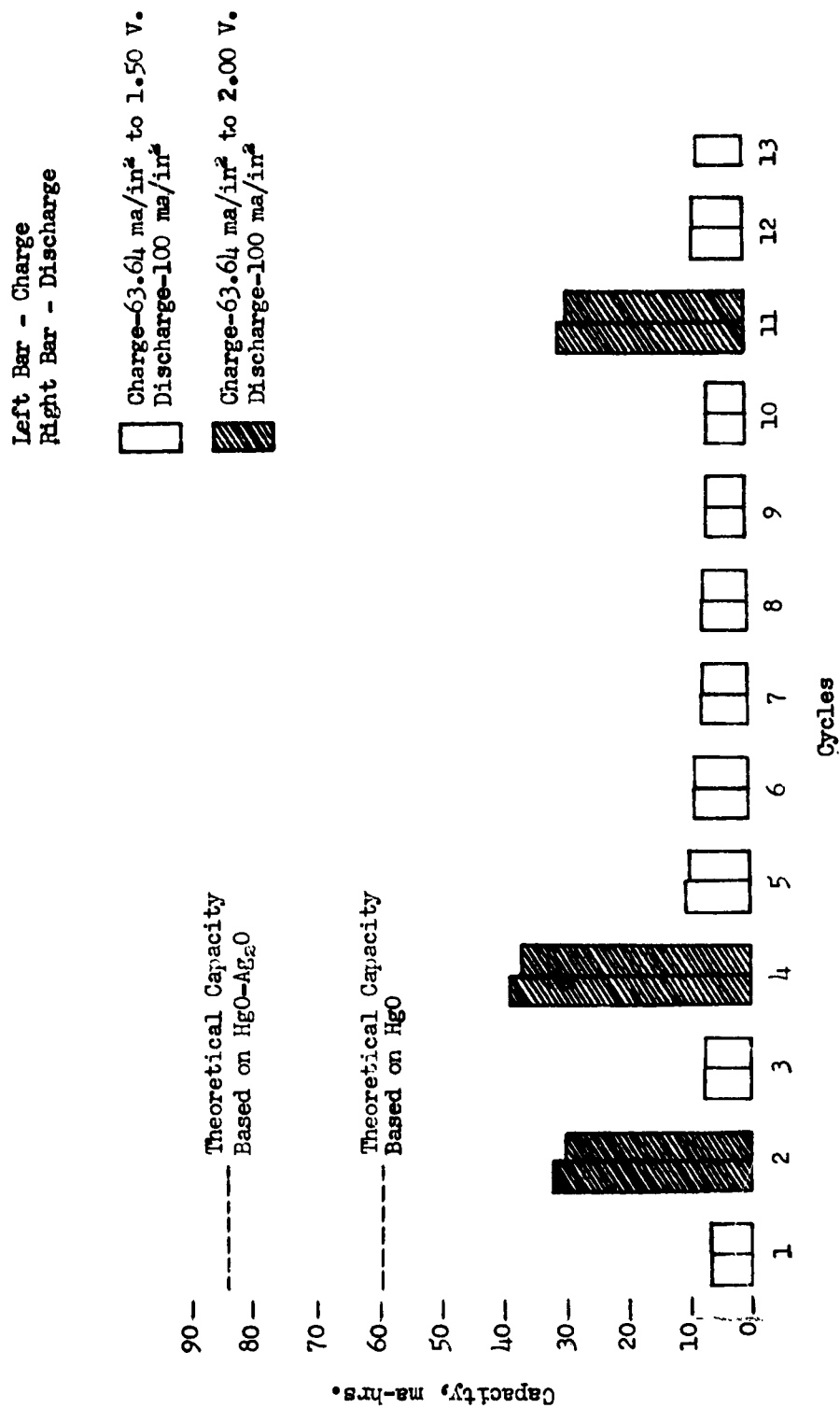


Figure 1 Positive Electrode of 31-69 Ag-Hg Alloy

Left Bar - Charge
Right Bar - Discharge

Charge-47.73 ma/in² to 1.50 V.
Discharge-75 ma/in²

Charge-63.64 ma/in² to 1.50 V.
Discharge-100 ma/in²

Charge-123.5 ma/in² to 2.00 V.
Discharge-300 ma/in²

Theoretical Capacity
Based on HgO-Ag₂O

Theoretical Capacity
Based on HgO

Capacity, ma-hrs.

- 6 -

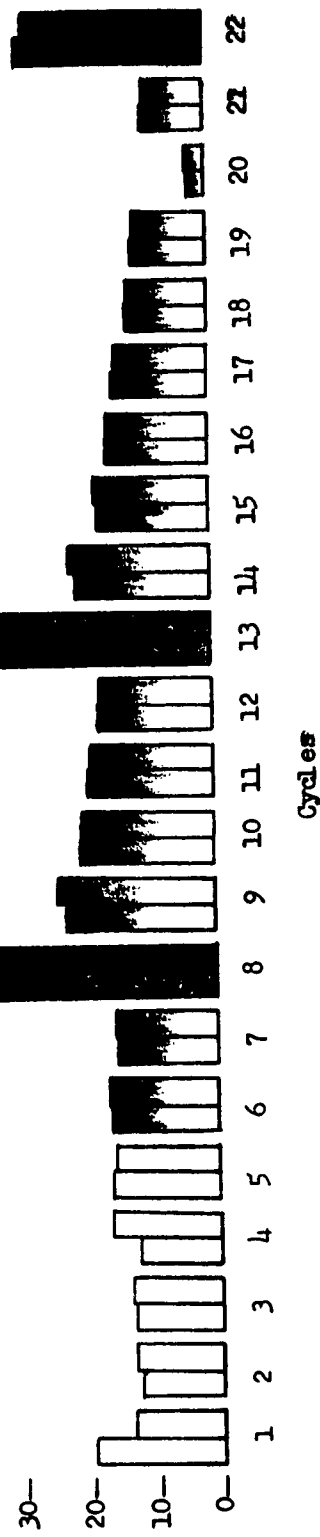


Figure 2 Positive Electrode with 0.3% Pd

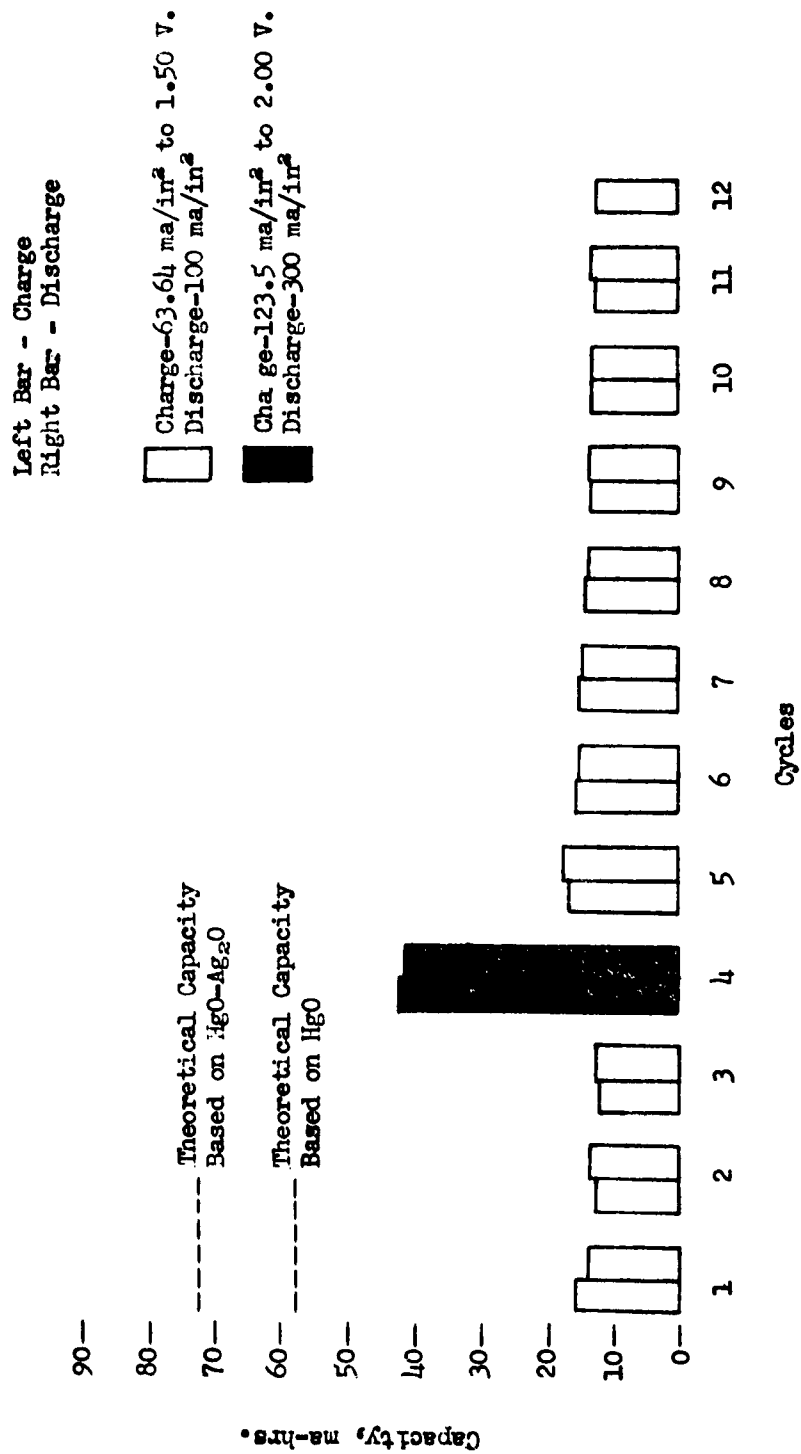


Figure 3 Positive Electrode with 0.65 Pt

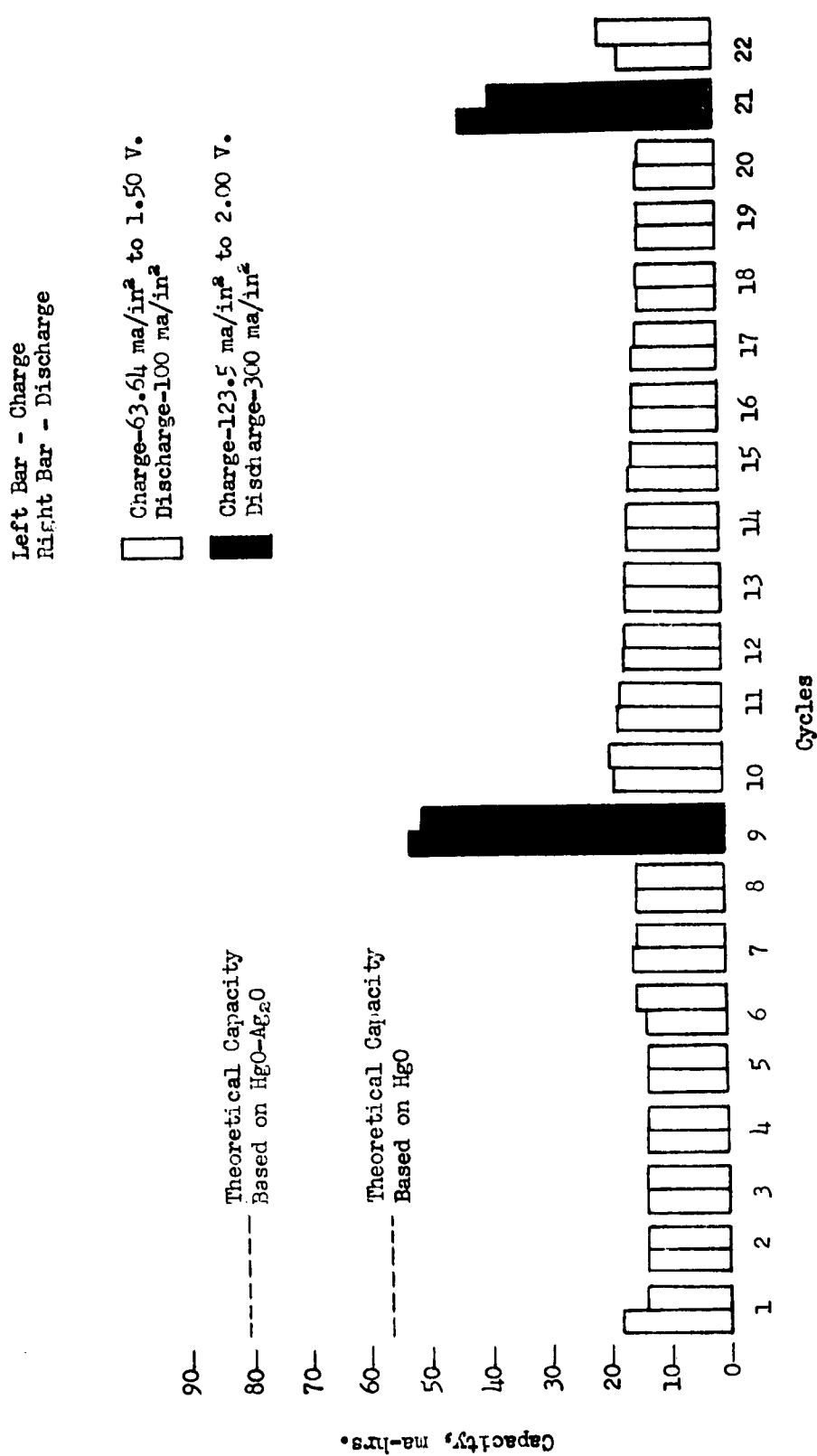


Figure 4 Positive Electrode with 0.13% Rh

Left Bar - Charge
Right Bar - Discharge

Charge-63.64 ma/in² to 1.50 V.
Discharge-100 ma/in²

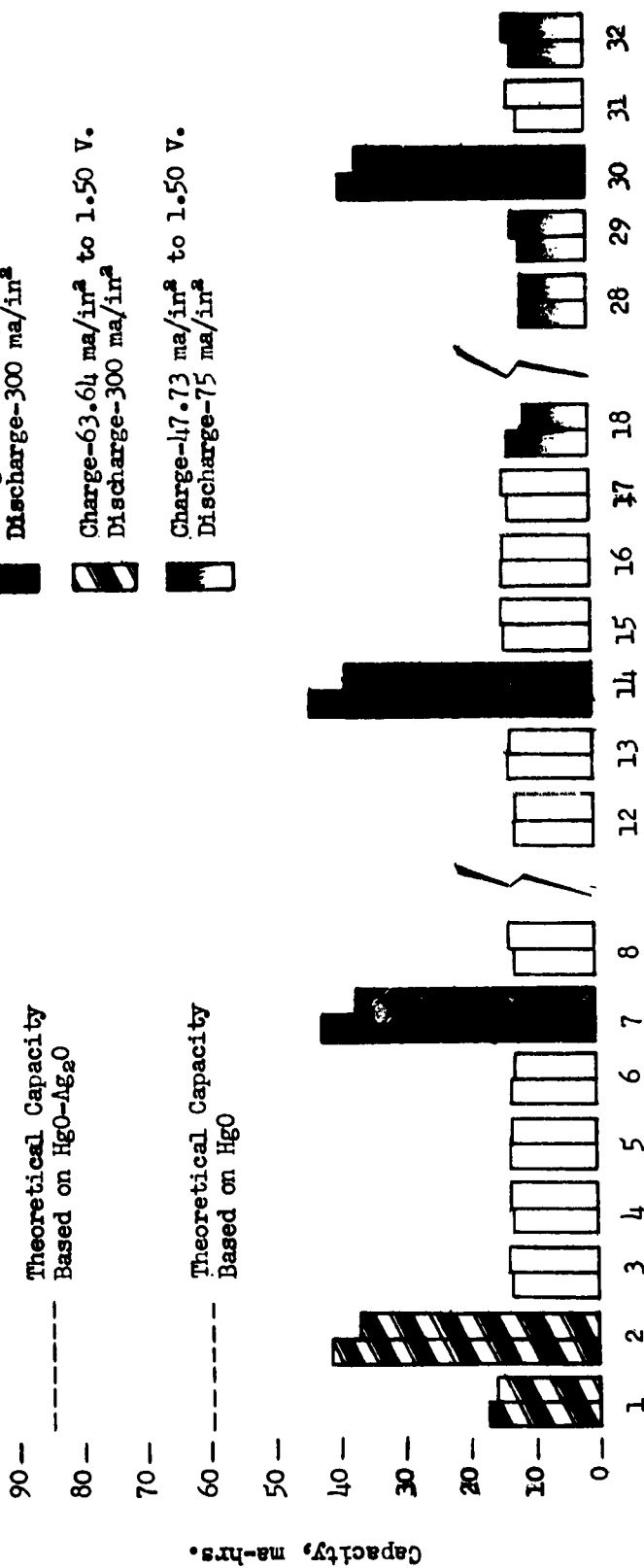
Charge-123.5 ma/in² to 2.00 V.
Discharge-300 ma/in²

Charge-63.64 ma/in² to 1.50 V.
Discharge-300 ma/in²

Charge-47.73 ma/in² to 1.50 V.
Discharge-75 ma/in²

Theoretical Capacity
Based on HgO-Ag₂O

Theoretical Capacity
Based on HgO



Cycles

Figure 5 Positive Electrode with 0.17% Pt and 2.0% Polyethylene Oxide

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